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FLUORESCENCE MONITORING OF CURING PROCESS AND WATER ACCESSIBILITY AT GLASS FIBER/EPOXY INTERPHASE ON COMPOSITE MATERIALS

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ABSTRACT

Modified glass fibers with three different amino silanes—(1) 3-aminopropyltriethoxysilane (APTES), (2) 3-aminopropylmethyldiethoxysilane (APDES), and (3) 3-aminopropyldimethylethoxysilane (APMES)—were la-beled with 5-dimethylaminonaphthalene-1-sulfonylchloride (DNS), and its fluorescence was followed as a function of curing time for two epoxide for-mulations (TRIEPOX-LM, Gairesa, Spain, and diglycidyl ester bisphenol A–ethylenediamine), as well as a function of water uptake. It was demonstrated that the fluorescence response from fluorophores directly attached to the cou-pling region in glass fibers/epoxy composites is a very sensible method for nondestructive and "in situ" monitoring of any changes that appear at the interphase (rigidity and solvent accessibility). In addition, fluorescence from a dansyl label shows more rigidity when APMES is used as the coupling agent. This suggests that the greater the cross-linking degree at the coupling region, the smaller the epoxy chain interdiffusion. Finally, the water uptake process in glass fiber/epoxy composites can be divided into two steps; the first step corresponds to the diffusion of water to the coupling region, and the second step corresponds to the hydrolysis of siloxane bonds in the inter-phase. Both steps are dependent on the surface treatment of the glass fibers.

KEYWORDS

Epoxy resin; Fluorescent labels; Glass fibers; Interphase; Si-lane treatment.

INTRODUCTION

A commonly accepted definition for composite materials corresponds to those formed by more than one component delimited physically from one another. When they are combined, there is a synergistic effect between their material properties. An example is glass fiber–reinforced epoxy composites, for which embedded high-modulus fibers in the epoxy polymer matrix increase mechanical properties of high-performance materials.

It is well known that properties of composite materials are strongly influenced by the type of adhesion between the reinforcement and the matrix [1–3]. If adhesion takes place, the interphase necessarily has to be controlled because (1) in many cases, the failure occurs in the interphase region and is caused by chemical reaction or plastification when impurities penetrate the interphase (commonly, water) [4-7]; and (2) composite materials depend on the ability of the interphase to transfer stress between the matrix and the reinforcement [8].

Surface treatment of reinforcement fibers has been a common method to improve general adhesion properties by increasing electrostatic interactions and facilitating chemical bonding between the components. Among others, coupling agents have a great effect on the interphase structure and properties [1,9]. They have two different functionalities, which can chemically bond with both the reinforcement and the matrix. The most commonly used coupling agents are difunctional organosilicon compounds called silanes. They have a general formula $Y\text{-}Si(X)_3$, where X is an alkoxy group or chlorine that, after hydrolysis to silanol, reacts with silanol groups present on the surface of the glass fibers to form siloxane linkages, and Y are nonhydrolyzable organofunctional groups such as amino, methacrylate, and the like that react with the matrix functional groups. In the case of epoxide-based composites, amino silanes are typical because of the possibility of amine hydrogen addition to the epoxide ring.

It is well known that, because of the chemical and structural differences in this coupling agent interphase layer, the mechanical properties of composite materials can be greatly changed [4,8,10], and different investigators have tried to explain the mechanisms responsible for enhancing mechanical properties in composites [1,8,11]. Nevertheless, in many cases, the interphase is not as well known as one would want. Due to this, for these systems it is necessary, among other things, to know (1) the extent of epoxy curing at the interphase because it will be related to its rigidity and molecular structure and (2) the accessibility of water to the interphase, as well as the effect that it produces. Both aspects are essential for better understanding of composite performance.

As far as we know, a great deal of research in this field has focused on

macroscopic characterization of composites by mechanical testing [4,8,11,12], giving to this research mainly a technological sense. Usually, different specimens are prepared by changing the surface treatment of the reinforcement, matrix formulation, curing polymer matrix conditions, and so on, or they are subjected to several processes of aging. After testing of the specimens, samples with mechanical properties more adequate for composite performance are selected.

The most common techniques used to investigate cure processes, such as differential scanning calorimetry, dynamic dielectric analysis, dynamic mechanical thermal analysis, and Fourier transform infrared (FTIR) report general information, while it will be of critical interest to monitor the curing just at the interphase. It is very difficult to find a very sensitive nondestructive technique that can give microstructural information at the interphase. Some attempts have been made, but although they can offer conclusive results, they present some difficulties derived from sample preparation, samples that are not very close to the real composites, interpretation of results, and the like [3,4,10].

Fluorescence is a very sensitive and nondestructive technique to monitor curing of different polymeric systems [13–17], and the use of fluorescent response from labels and probes is becoming a very powerful tool to follow changes in surroundings such as polarity and/or microviscosity [13–20].

Recently, Yu and Sung [21] proposed the use of a fluorescence technique to provide chemical information during cure at the fiber/polymer matrix interphase. They followed the spectral shift in the fluorescence of a commonly used aromatic diamine hardener. Using this method, they could see the influence of different surface treatments of fibers on curing extent of the polymer matrix, but because of some instrumental difficulties, this approach cannot be used as an online "in situ" method for monitoring the epoxide curing just at the interphase.

Some fluorescent molecules, such as dansyl derivatives, show an appreciable shift in their fluorescence emission band depending on the polarity and/or rigidity of their surroundings [15,22,23]. Therefore, they are good candidates as fluorescence labels or probes to monitor any change that appears in polymeric systems.

In this work, it was proposed to use the fluorescent response of dansyl groups directly attached to the coupling region between the reinforcement and the matrix to follow the curing process of the polymer and water accessibility as a function of different surface treatments of glass fibers, in both cases just in the interphase.

EXPERIMENTAL

Sample Preparation

Dansyl Labeling of Glass Fibers

Three different amino silanes were supplied by Aldrich Company (Madrid, Spain): 3-aminopropyldimethylethoxysilane (APMES), 3-aminopropylmethyl-

diethoxysilane (APDES), and 3-aminopropyltriethoxysilane (APTES). These silanes were labeled with 1-dimethylamino-5-naphtalenesulfonilchloride (Lancaster Synthesis, Ltd., Bischheim, France). The fluorescence label, dansyl chloride, reacts easily with amino groups of aminosilanes, yielding sulfonamide fluorescent derivatives (DNA). The stoichiometry of the reaction was 1:1000 (dansyl: NH_2).

Glass Fiber Surface Pretreatment

1. Commercial E-glass fibers were obtained from Vetrotex (Madrid, Spain) and were cleaned by heating at 450°C for 1 h to remove any organic substance from the surface. 2. After that, the fibers were chemically coated with a dansyl-labeled aminosilane coupling agent. This was done by immersing 1 g glass fibers in 50 mL of silane 1% (vol/vol) aqueous solution for 10 min at room temperature. Three different molecular structures of the silane coatings were obtained by using the silane coupling agents with the different functionalities mentioned above.
3. After squeezing the fibers, the adsorbed silane was cured at 110°C for 1 h to accelerate the condensation reaction and to remove water.
4. Silanized and dansyl-labeled glass fibers were subjected to a soxhlet extraction with dry toluene for at least 4 h to remove all physisorbed residues, and then they were vacuumed for at least 8 h.

Epoxy Mixture Preparation

Two epoxy mixtures were prepared. The first one was a commercial system, type code TRIEPOX, supplied by Gairesa Company (Lugo, Spain), and the second one was taken as a model system. The TRIEPOX system was prepared by mixing the first component (high functionality epoxy resin, degassed before use) and second component (cycloaliphatic amines) in a weight proportion of 2.34/1. The model system was prepared by the mixing the first component (diglycidyl ether of bisphenol A [DGEBA], obtained from Aldrich Co., Madrid, Spain, and degassed before use) and second component ethylenediamine (EDA; Aldrich Co.) in the stoichiometric ratio.

Specimens for water accessibility studies were prepared as follows: A mold was made using an adhesive Teflon sheet with a hole in it. Bundles of fibers with different coatings were glued across the hole to the adhesive face of the Teflon sheet lying on a Teflon plate. After that, the hole was filled with the DGEBA/EDA epoxide mixture and sealed with another Teflon plate. The epoxide system was cured at 90°C for 24 h and postcured at 115°C for 4 h. This

curing procedure was selected to ensure that at least 98% epoxy group conversion was achieved.

Dansyl Labeling of the Epoxide Components

Preparation of a reactive dansyl derivative 5-dimethylaminonaphtalene-1-(2-aminoethyl)sulfonamide (RDNS) used for labeling of diepoxide (DGEBA) has been described elsewhere [24]. Labeling of the epoxide components by reaction with reactive dansyl derivative (RDNS) was carried out by heating both components under stirring at 60°C for 6 h, as also described elsewhere [24].

Analysis Methods

Steady-state fluorescence spectra were taken on two fluorimeters. The first, a fluorimeter LS 50B (Perkin Elmer Ltd., Beaconsfield Bucks, UK), was used for dansyl-labeled model systems without fibers. Fluorescence from samples of dansyl-labeled epoxide mixtures was followed by using front-face geometry in home-made thermostated cuvettes. The second, an Edingburg fluorimeter (Edinburg, UK), was used for dansyl-labeled glass fibers in the composites. An optical fiber cable was used to excite and collect in situ fluorescence. In both cases, the excitation wavelength was set at 360 nm, and the spectra were recorded from 375 to 700 nm using excitation and emission slits of 3 nm.

For the water accessibility study, the different specimens were immersed in bidistilled water at room temperature, and dansyl fluorescence from the interphase was taken for several immersion times. On the other hand, for each immersion time, the contribution of epoxy emission was subtracted. It was necessary to do this because, when APMES is used as the silane coupling agent, the fluorescence from dansyl-labeled glass fibers was very low.

RESULTS AND DISCUSSION

Fluorescence Monitoring of Curing

To compare the difference between the curing process at the glass fiber/epoxy matrix interphase and curing in the bulk polymer model system, the fluorescence response of the dansyl coupling agent label was followed as a function of curing time. The band shift in the maximum $\Delta\nu$ (cm^{-1}) was selected from the emission spectra for comparison. This parameter was taken to eliminate errors that come from the use of different equipment.

In Fig. 1, the change in the band shift as a function of cure time is shown for the dansyl-labeled polymer model system (sample A), the composite with

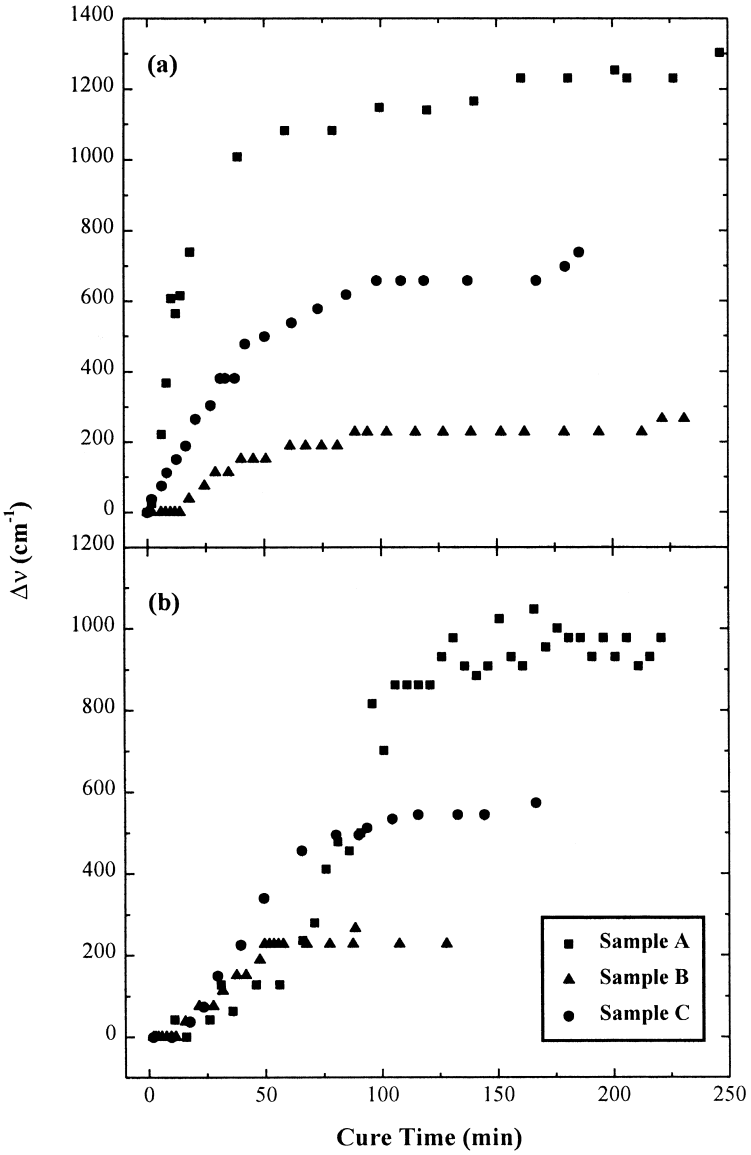

Figure 1. Variation of band shift as a function of cure time for the dansyl-labeled polymer model system (sample A), composite with APTES-coated glass fibers (sample B), and composite with APDES-coated glass fibers (sample C): (a) TRIEPOX; (b) DGEBA/EDA.

APTES-coated glass fibers (sample B), and the composite with APDES-coated glass fibers (sample C). The TRIEPOX resin and DGEBA/EDA reaction mixture results are plotted in Fig. 1a and 1b, respectively. The three systems showed a similar pattern (samples A, B, and C). There was a fast increase at the beginning of the curing process, and the systems reached a plateau at longer curing times. Nevertheless, a faster shifting of the emission band is clearly seen for the model polymer system. This observation can be interpreted as a slower reaction rate at the interphase of the composites. It is well known that reaction rates of polymerization processes are greatly decreased when free volume is reduced [25]. In addition, it is true that the epoxide reaction mixture will have less free volume in the coupling region of composites than in the bulk of the polymer. Therefore, when the dansyl group is chemically bonded to the silane coupling layer, its excited state will be affected by slower changes in the epoxide reaction mixture.

Using the same argument, one could explain the differences observed between samples B and C. In sample B, a higher cross-linking density is expected in the coupling region because a trifunctional silane was used as the coupling agent, while for sample C, a difunctional silane was used. Therefore, for sample B, one can expect a slower increase in the shift of the emission band, as was actually obtained.

Other parameters that can be used to analyze the epoxy curing process are the integrated intensity and the wavenumber of the emission band maximum, as can be seen from the effect of different molecular structures at the interphase of glass fibers/epoxy matrix composites in Fig. 2 and 3.

In general, fluorophores that, following absorption of excitation light undergo nonradiative decay by intramolecular twisting or torsional motions such as aminonaphtalenes [26] like dansyl derivatives [27], show a viscosity-dependent fluorescence [16,28]. When epoxy curing takes place, the motion of the fluorophores becomes progressively more inhibited by increasing viscosity of the polymer. Higher viscosity leads to a gradual increase in the intensity of fluorescence.

For the DGEBA/EDA system (Fig. 2), the fluorescence intensity shows nearly the same profile with curing time when fibers are coated with APTES and APDES. The intensity greatly increased during the first stage of the curing process and reached a plateau at longer reaction times, suggesting that rigidity at the interphase follows the same tendency. Nevertheless, this parameter is not quite sensitive enough to reflect differences between the two samples.

On the other hand, the energy of the emission band experienced different changes with curing depending on the coupling region (Fig. 2b). As curing progressed, there was a blue shift in the emission band of the dansyl label that is lower when the glass fibers were coated with APTES. It is known that the dansyl emission band undergoes a blue shift when the viscosity increases [24,29]; therefore, Fig. 2b suggests that, when glass fibers are coated with APDES, the epoxy curing at the interphase goes faster and leads to a more rigid structure. The former observation was interpreted above, while the latter can be explained in the following way. Since the accessibility of epoxy groups of the polymer to

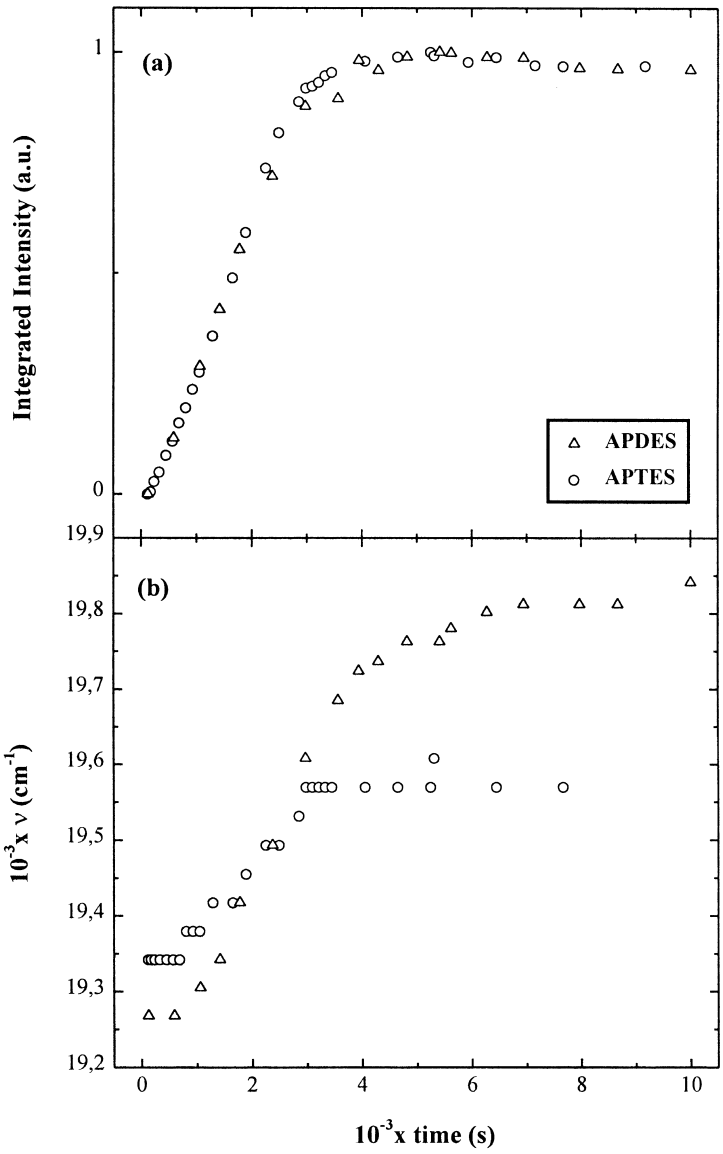

Figure 2. (a) Integrated fluorescence intensity and (b) the wavenumber at the emission maximum as a function of curing time for glass fiber/(DGEBA/EDA) system. Effect of glass fiber pretreatment.

amino groups of the glass fiber coatings depends on their molecular structures, the greater accessibility of the amino groups (less cross-linking density of the organosiloxane layer), the higher the cross-linking density in the interphase and, therefore, the higher rigidity as was obtained.

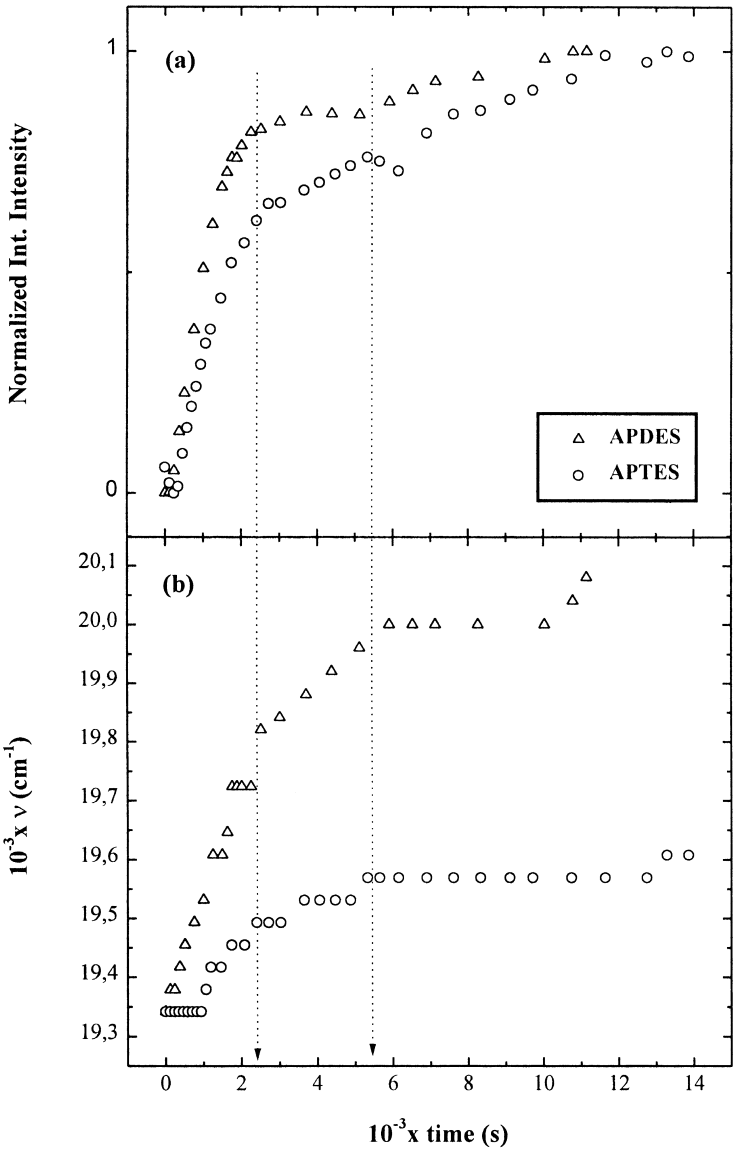

Figure 3. (a) Integrated fluorescence intensity and (b) the wavenumber at the emission maximum as a function of curing time for glass fiber/(TRIEPOX) system. Effect of glass fiber pretreatment.

From Fig. 3, nearly the same observations can be extracted, but now for the TRIEPOX system. Nevertheless, for the TRIEPOX system, the integrated intensity increased differently with curing time depending on silane coating. In Fig. 3a, two regions can be observed: (1) the first stage of curing, with a large

increase in fluorescence intensity, and (2) longer curing times, with little increase in intensity. In the former region, the fluorescence intensity increased faster when APDES was used as the coupling agent, while in the latter region, the intensity increased faster when APTES was used. These results seem to the corroborate the explanations given. If epoxy groups have more ability to interdiffuse though the coupling region to reach amino groups easily when APDES is used, the curing rate has to be higher, as observed.

Another general observation that can be made is that the energy of the dansyl emission band changed, with curing time, much more than the fluorescence intensity. Therefore, that parameter seems to be more powerful.

Fluorescence Monitoring of Water Accessibility to the Interphase

The wavenumber at the emission maximum of the dansyl label as a function of immersion time in water at room temperature is shown in Fig. 4. The

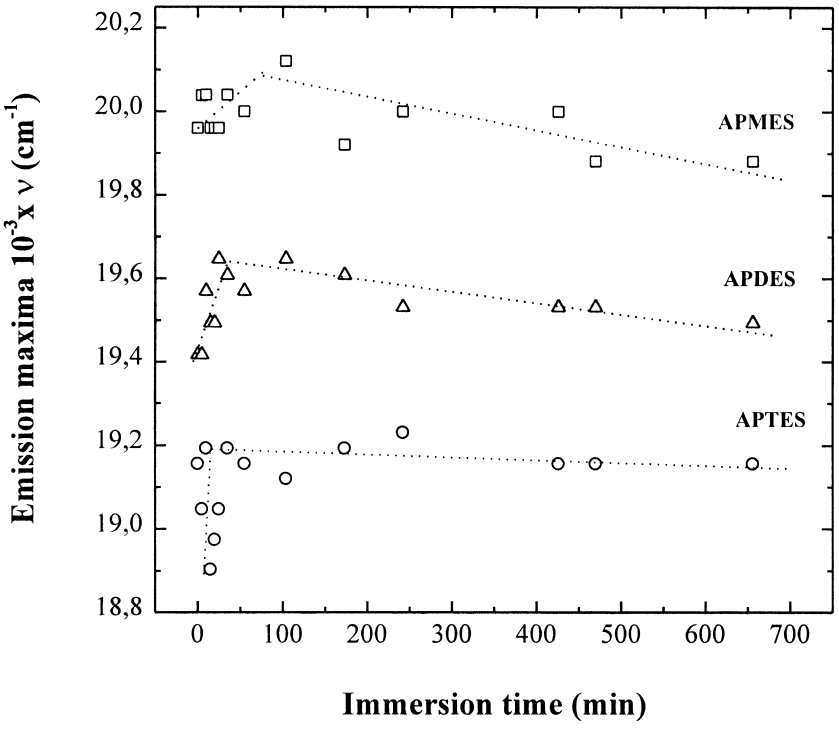

Figure 4. Wavenumber at the emission maximum of dansyl label as a function of immersion time in water at room temperature.

effect of glass coating (APMES, APDES, and APTES) on the water uptake of glass fiber/epoxy composites was studied. It is observed that the blue shift of the dansyl label emission band, with respect to the silane coatings, was in the order APMES > APDES > APTES. Therefore, considering the above-mentioned arguments, the rigidity at the interphase must follow the same order. Furthermore, Fig. 4 shows two regions for the three specimens studied (accessibility region and hydrolytic region). During the first minutes of immersion (about 100 min), there was an increase in the wavenumber at the emission maximum of dansyl fluorescence, while for longer times, a decrease was observed. The tendency seen in the first region might be due to a hydrophobic effect provoked by water when it reached the coupling region because that region is formed by very hydrophobic siloxane bonds. The cavity in which the dansyl fluorophore is immersed can be reduced due to that hydrophobic interaction, yielding a blue shift in its fluorescence emission. On the other hand, the tendency observed in the second region must be due to hydrolysis of siloxane bonds in the interphase. If siloxane bonds hydrolyze, silane oligomers and/or monomers can diffuse through the interphase, acting as plasticizers and therefore increasing the dansyl label mobility. If that occurs, the dansyl emission band would shift to the red, as observed in Fig. 4.

Comparing the results from the composites studied, one can observe that the slopes in both the accessibility and hydrolytic regions depend on the glass surface treatment. The accessibility region has a larger slope with a higher cross-linking density of the coupling layer (APTES), while for the hydrolytic region, the larger slope corresponds to the higher probability to produce monomers that can more easily plasticize the interphase (APMES).

CONCLUSIONS

- The fluorescence response from fluorophores directly attached to the coupling region in glass fibers/epoxy composites is a very sensitive, nondestructive, and in situ method to monitor any changes that appear at the interphase (rigidity, polarity, solvent accessibility).
- Among the photophysical parameters, the energy of the emission band seems to be the most powerful for characterizing the changes in the epoxy-based systems.
- Fluorescence from the dansyl label showed more rigidity for the interphase when APMES is used. This suggests that there is greater cross-linking density in the coupling region as the epoxy chain interdiffusion decreases.

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